



MTC 6610
39-21(3631C)
PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of Jerry R. Ebner, et al.

Art Unit 1623

Serial No. 09/408,323

Filed September 29, 1999

For DEEPLY REDUCED OXIDATION CATALYST AND ITS USE

IN PREPARING N-(PHOSPHONOMETHYL)GLYCINE COMPOUNDS

Examiner L. Maier

July 3, 2001

THIRD SUPPLEMENTAL
INFORMATION DISCLOSURE STATEMENT

In accordance with 37 C.F.R. §1.97, and in compliance with 37 C.F.R. §1.56, applicants herewith submit this Third Supplemental Information Disclosure Statement, including the an additional reference that is listed on attached PTO form 1449.

Information is provided hereinbelow regarding the opposition filed by Monsanto Company to Nitrokemia EP 0 019 445, one of the references cited in the PTO 1449 form.

This Statement also provides information on commercial batch process operations conducted by Applicants' assignee for the oxidation of N-(phosphonomethyl)iminodiacetic acid to N-(phosphonomethyl)glycine (hereinafter "glyphosate"), and provides further information on a process proposed by a third party for a continuous process for the oxidation of N-(phosphonomethyl)-iminodiacetic acid to glyphosate.

Further disclosed is information determined by Applicants regarding the C/O surface ratio of a catalyst prepared in accordance with Chou US patent 4,696,772, and CO desorption characteristics of both the Chou catalyst and a catalyst as

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prepared in accordance with Kim et al. *J. Electrochem. Soc.*, Vol.
140, No. 1, pp. 31-36.

Commercial Batch Process

A number of US patents of Monsanto Company already of record in this application are generally descriptive of batch processes carried out prior to the present invention, and/or more than a year before the priority date of the instant application, for the oxidation of N-(phosphonomethyl)iminodiacetic acid to glyphosate using a carbon catalyst. No prior art commercial batch process as practiced by Monsanto Company for oxidation of N-(phosphonomethyl)iminodiacetic acid to glyphosate has used a noble metal catalyst in any form. All such processes have used carbon, and carbon only, as the catalyst for the reaction.

Prominent among the patents describing batch processes of the type practice commercially by Monsanto are Hershman US 3,969,398, relied on by the Examiner in the Office action of January 11, 2001, and Chou US 4,696,772. A carbon catalyst prepared substantially as described in Chou US patents 4,624,937 and 4,696,772, and representative of the type used in a commercial batch process for the preparation of glyphosate, has been found to exhibit a carbon monoxide desorption of 0.11 to 0.23 mmol CO/g catalyst when a dry sample of the catalyst is heated in a helium atmosphere from about 20 to about 900°C at a rate of about 10°C per minute, and then at about 900°C for about 30 minutes. The same carbon catalyst was found to have a ratio of carbon atoms to oxygen atoms of approximately 30:1 at the surface as measured by x-ray photoelectron spectroscopy.

Nothing in the aforesaid commercial batch operation suggests the use of a noble metal on carbon catalyst, as called for in all the pending claims. The batch operation further fails to teach

or suggest the use of a deeply reduced noble metal on carbon catalyst as specified in claims 1-52, 66-99 and 150-199. Since the catalyst used in the batch process consisted entirely of carbon, the problems presented in preparation and use of the carbon catalyst differed from the problems presented in developing a noble metal catalyst in which carbon provides a support for the noble metal. By way of significant example, the commercial batch process was not confronted with the problem of noble metal dissolution.

Also, the carbon only catalyst is not nearly as effective as a noble metal on carbon catalyst for the oxidation of C_1 by-products of the oxidation reaction, i.e., formaldehyde and formic acid.

In certain of the commercial batch processes operated in the United States for more than a year before the priority date of this application, the oxygen flow rate to the carbon-catalyzed reaction mass has been progressively reduced beginning at a point in the cycle at which significant conversion has been reached. However, the purpose and effect of reducing oxygen flow in the batch carbon catalyzed reaction differs in at least one important respect from the purpose and effect of reducing flow in the last reaction zone of a continuous process. Reducing the flow rate in the second continuous reactor containing a noble metal on carbon catalyst prevents over-oxidation of the noble metal, thereby preserving its effectiveness for promoting the C_1 oxidation reaction and minimizing loss of metal by dissolution.

It has further been observed that the oxygen utilization in what is believed to be a typical commercial batch operation more

than a year before the filing date of the instant application was below 60%. As specified in claims 7 to 9 and 125-127 call for an oxygen utilization in excess of 60%. Observation of commercial operation of the claimed continuous process of claims 100-199 shows that oxygen utilization well above 60% is achieved.

It further has been observed that, in the carbon-catalyzed commercial batch process as conducted by Applicants' assignee, the oxidation of N-(phosphonomethyl)iminodiacetic acid to glyphosate proceeds as a substantially zero order reaction until a high conversion is achieved. Assuming *arguendo* that the observed kinetic behavior of the carbon-catalyzed oxidation is part of the prior art, it is respectfully submitted that the kinetic behavior of a reaction as catalyzed by carbon only would not necessarily provide a basis for predicting the kinetics of that reaction as catalyzed by a noble metal on carbon. Under the applicable standards of §103, the operation of the commercial batch process in the manner observed does not render obvious the instantly claimed continuous process in which the catalyst comprises a noble metal on carbon.

Prior to the present invention, noble metal on carbon catalysts had never been used in a manufacturing facility by Applicants' assignee except in one experimental run with a Pt/C catalyst wherein catastrophic loss of platinum was suffered. According to the instant invention, the effective use of a noble metal on carbon catalyst has been an instrumental factor in enabling Applicants to successfully conduct the oxidation reaction in a continuous fashion. Nothing in the combination of the commercial batch process with any other art of record would

have made a continuous process according to the instant claims obvious to one skilled in the art.

The commercial batch process further failed to provide any basis for the discovery that deeply reduced noble metal on carbon catalysts would substantially reduce metal loss and would be commercially effective for the conversion of N-(phosphonomethyl)iminodiacetic acid to glyphosate with minimal loss of noble metal. Nor does the commercial batch operation suggest that use of a noble metal on carbon catalyst would be especially effective for the carrying out the process in a continuous mode.

In view of the above considerations, it is respectfully submitted that claims 1-199 distinguish patentably over any combination of the batch process and the prior art of record.

Third Party Proposal for Continuous Oxidation

Prior to the development of the deeply reduced noble metal on carbon catalyst, one of the inventors herein conceived a continuous process for the manufacture of glyphosate by oxidation of N-(phosphonomethyl)iminodiacetic acid in the presence of a carbon catalyst in a continuous stirred tank reactor (CSTR). The process as conceived proposed a single CSTR for partial conversion of N-(phosphonomethyl)iminodiacetic acid to glyphosate, after which the carbon catalyst was to be removed by filtration, glyphosate was to be recovered by crystallization, and both the catalyst and the crystallization mother liquor containing unreacted N-(phosphonomethyl)iminodiacetic acid were to be recycled to the CSTR. Contemporaneously with this

conception, Applicants' assignee, Monsanto Company, learned of a different reactor of unique design that was believed to have possible application in the continuous process as conceived by the inventor.

Accordingly, contact was established with an outside third party that was the source of the technology in the unique reactor. Monsanto provided to the third party a confidential disclosure of the continuous process utilizing a carbon catalyst as had been conceived by the aforesaid inventor and outlined above. After receiving this disclosure, the outside third party made a proposal to Monsanto for a continuous process which was generally based on the Monsanto disclosure but used the unique reactor configuration.

The third party made the proposal to Monsanto in confidence, so Monsanto is not at liberty to disclose the identity of that party. While the applicable confidentiality agreement may no longer impose a confidentiality obligation on Monsanto with regard to the substance of the disclosure, as a matter of caution and deference to the outside party Monsanto prefers not to identify the nature of the unique reactor. It has never been used even experimentally by Applicants herein, or by Monsanto, in the oxidation of N-(phosphonomethyl)iminodiacetic acid to glyphosate.

However, without violating any confidences, several observations can be made about the process as proposed by the outside party. It was not possible to determine from the proposal whether the reactor was to be operated in a fully back mixed, predominantly back mixed, or predominantly plug flow condition.

The proposal also failed to describe the conditions of operation in the reactor other than temperature. The proposed reaction temperatures differed from the preferred temperatures as described in the instant application, and were commercially unattractive to Monsanto. From a flow sheet provided in the proposal, Monsanto engineers inferred that the third party contemplated a quantitative conversion of N-(phosphonomethyl)-iminodiacetic acid to glyphosate, but no conversion data or material balances were provided. Because only a carbon catalyst was contemplated for the reaction, it appeared to Monsanto that the process could have been rendered infeasible (or in any case, unacceptable) by an accumulation of by-product formaldehyde and formic acid in the reaction system and reaction thereof with glyphosate to provide undesirable glyphosate derivatives such as N-methyl glyphosate. The flow sheet proposed to remove formaldehyde and formic acid from the reaction system by circulating reaction mixture between the reactor and a flash tank, which would also serve to remove some reaction heat. However, there were no data or calculations in the proposal relating to kinetics or separations, and no material balances, from which Monsanto personnel who reviewed the proposal could determine whether C₁ by-products would be reduced to an acceptable level by the scheme proposed.

No experimental or theoretical evidence was offered by the outside party to establish that the process could be operated to produce a reaction product from which glyphosate could be satisfactorily recovered without excessive formation of by-products. Nor were there data establishing that the indicated

quantitative conversion could or would be achieved within a commercially reasonable or acceptable residence time, though the latter may well have been possible. The flow sheet provided with the proposal was purely conceptual. So far as Monsanto is aware, the outside party never attempted to experimentally demonstrate the process as proposed. The disclosure did include steps for recovery of glyphosate from the reaction mixture, and also suggested certain stratagems for recovery of process heat. None of these are relevant to the instant invention as claimed herein.

Kim et al., J. Electrochem. Soc., Vol. 140, No. 1, pp. 31-36

Kim et al. *J. Electrochem. Soc.* article disclose a reduced Fe-Pt on carbon catalyst and its experimental use for oxygen reduction in phosphoric acid fuel cells. Kim et al. heat this catalyst in H₂ for 3 hours at 450°C, and then in Ar for 2 hours at 450, 750, or 900°C. Kim et al. fail to teach or suggest that their catalyst yields less than 1.2 mmole of CO per gram of catalyst according to the protocol of claim 1 wherein the catalyst is first heated at a temperature of about 500°C for about 1 hour in a H₂ atmosphere. However, Applicants have prepared a Pt/C catalyst using the method described on page 32 of Kim et al.'s disclosure, tested it by the claim 1 protocol, and found that Kim et al.'s catalyst yielded 0.503 and 0.509 mmoles of CO per gram of catalyst.

Despite these experimental findings by Applicants, who were motivated to test Kim only in the light of Applicants own invention, the Kim et al. reference remains lacking in any teaching regarding the CO desorption characteristics of the

catalyst which the authors prepared. Consequently, the reference creates no basis for obviousness of the process of claim 1 wherein N-(phosphonomethyl)iminodiacetic acid is oxidized to glyphosate using a catalyst exhibiting a CO desorption that is very low, even though somewhat higher than the apparently inherent CO desorption characteristic of Kim's catalyst. Obviousness cannot be predicated on what is unknown; *in re Spormann*, 150 USPQ 449, 452 (CCPA 1966).

Kim et al. present no teaching or suggestion of the use of their catalyst in reactions such as those claimed in the instant application. As noted, the only use disclosed by Kim is for oxygen reduction in a phosphoric acid fuel cell.

EPO 0 019 445

Attached Nitrokemia EP patent 0 019 445 describes and claims a process for conducting a batch oxidation of N-(phosphonomethyl)-iminodiacetic acid substrate ("PMIDA") in the presence of a noble metal on carbon catalyst wherein the charge mixture initially contains particulate PMIDA suspended in an apparently saturated aqueous solution thereof. The total initial concentration of PMIDA in the suspension is at least 7 g PMIDA per 100 ml water. The Nitrokemia patent contains no suggestion that the catalyst should be subjected to reductive treatment to eliminate surface oxides, and in fact fails to recognize the noble metal dissolution problem that would make the disclosed process commercially infeasible if practiced with a noble metal on carbon catalyst.

Nitrokemia also fails to suggest conducting the oxidation of PMIDA in a continuous mode. Moreover, the patent contends that higher specific conversions of PMIDA to glyphosate are achieved in a batch reaction by starting with a suspension rather than an unsaturated, or even saturated, solution of PMIDA in the aqueous medium. Although the patent contains no discussion of kinetics as such, the Nitrokemia contention regarding specific conversion would appear consistent with an expectation that the reaction rate depends on the integrated average substrate concentration in the aqueous phase, i.e., that the reaction would behave in accordance with first order, or at least other than a zero order, kinetics. In this respect Nitrokemia leads away from the process of claim 100 since one skilled in the art would expect unsatisfactory productivity from conducting a first order reaction in a continuous stirred tank reactor ("CSTR"), which typically operates under substantially back-mixed terminal conditions in which the steady state concentration of PMIDA is very low. The Nitrokemia text confuses the issue by stating that the reaction in a suspension system may take place only at the boundary surfaces, without making it clear what "boundary surfaces" are contemplated. But whatever the implications of the latter teaching, Nitrokemia certainly would not lead one skilled in the art to the CSTR based process of claim 100.

Monsanto, the assignee of the instant application, opposed the Nitrokemia patent application in Europe and a corresponding application in Australia, arguing that the reaction rate is dependent only on catalyst concentration, and that no benefit in conversion is actually achieved by starting with a suspension of

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N-(phosphonomethyl)iminodiacetic acid in a saturated solution thereof. Monsanto submitted an affidavit which presented data showing that conversion rate is a linear function of catalyst concentration using a carbon catalyst at concentrations of 0.8 to 1.2% by weight and a starting substrate concentration of 7.3 g per 92 ml water. Based on this data, the affidavit concludes that changes in "specific conversion" value can be obtained simply by increasing the catalyst charge at a given temperature and pressure, regardless of the concentration of starting material. However, it is not stated on the record of either the EPO or Australian oppositions that the reaction is zero order. The order of the reaction is not discussed.

Accordingly, it is respectfully submitted that neither the Nitrokemia patent nor the contentions made in the aforesaid oppositions, whether taken alone or together with any prior art of record, would lead to the process as defined in any of the pending claims.

Conclusion

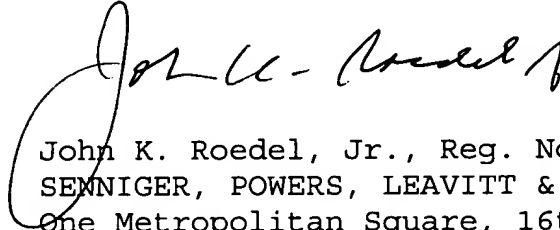
It is, therefore, respectfully submitted that claims 1-199 distinguish patentably over the proposal of the outside third party, or any combination thereof with the art of record and/or the commercial batch operation as further described hereinabove.

A check in the amount of \$1,934.00 is enclosed to cover the fee specified in 37 CFR §1.17(p) for submission of this Information Disclosure Statement, a three-month extension of time and additional claims. The Commissioner is hereby authorized to

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charge any additional fees required under 37 CFR 1.16 and 1.17 or
refund any overpayment to Deposit Account No. 19-1345.

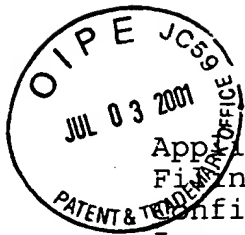
Respectfully submitted,



John K. Roedel, Jr., Reg. No. 25,914
SENNIGER, POWERS, LEAVITT & ROEDEL
One Metropolitan Square, 16th Floor
St. Louis, Missouri 63102
(314) 231-5400

JKRmkd

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Application Number 09/408,323
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Inventor(s) Jerry R. Ebner et al.
Group Art Unit 1623
Examiner Name L. Maier
Attorney Docket Number MTC 6610 (39-21(3631D))

METHOD OF PAYMENT

1. ☐ The Commissioner is hereby authorized to charge the indicated fees to Deposit Account No. 19-1345.
- ☒ The Commissioner is hereby authorized to charge any additional fees required under 37 CFR 1.16 and 1.17 to Deposit Account No. 19-1345.
- ☐ Applicant claims small entity status.
2. ☒ Check Enclosed. The Commissioner is hereby authorized to charge any under payment or credit any over payment to Deposit Account No. 19-1345.

FEE CALCULATION

1. ☐ BASIC FILING FEE Subtotal (1) \$ _____
(Type: _____)
2. ☒ EXTRA CLAIM FEES Subtotal (2) \$ 864.00
- Total Claims 247 (199 previously paid for)
Independent Claims 8 (8 previously paid for)
Multiple Dependent Claims _____
3. ☒ ADDITIONAL FEES Subtotal (3) \$ 1,070.00
- ☐ Surcharge - late filing fee or oath
☐ Surcharge - late provisional filing fee or cover sheet
☒ Extension for reply within three months
☐ Notice of Appeal
☐ Filing a Brief in Support of an appeal
☐ Request for ex parte Reexamination
☐ Petitions to the Commissioner
☒ Submission of Information Disclosure Statement
☐ Recording each patent assignment per property
☐ Request for Continued Examination
☐ Other: _____

TOTAL AMOUNT OF PAYMENT \$ 1,934.00

John K. Roedel, Jr.
John K. Roedel, Jr., Reg. No. 25,914

July 3, 2001
Date

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